

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
30 October 2003 (30.10.2003)

PCT

(10) International Publication Number  
**WO 03/089108 A1**

- (51) International Patent Classification<sup>7</sup>: B01D 19/04. C11D 3/42. 3/00
- (21) International Application Number: PCT/EP03/03727
- (22) International Filing Date: 10 April 2003 (10.04.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
02405320.9 19 April 2002 (19.04.2002) EP
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- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CI, CG, CL, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
- with international search report
  - before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 03/089108 A1

(54) Title: FOAM CONTROL AGENTS

(57) Abstract: This invention relates to a particulate foam control agent comprising (a) from 1 to 30 parts by weight of a silicone antifoam; (b) from 45 to 99 parts by weight of a particulate carrier for the antifoam, (c) from 2 to 50 parts by weight of a fluorescent whitening agent; (d) from 1 to 40 parts by weight of a binder.

### Foam Control Agents

This invention relates to particulate foam control agents comprising a fluorescent whitening agent (FWA), more particularly those intended for incorporation in detergent compositions which are in powder form.

Optical brighteners, also known as fluorescent whitening agents, are commonly used in laundry detergents. Brighteners deposit onto fabrics where they absorb ultraviolet radiant energy and reemit it as a blue light. This reduces or eliminates any yellowish cast to fabrics and gives them a brighter appearance. It is often desirable to add the fluorescent whitening agents in post addition processes by dry blending with granules that contain all the FWA amount. However, undesirable brightener staining on fabrics can occur when the post added granules come in direct contact with wet cotton-containing fabrics.

It was now found that such staining can be reduced or eliminated while maintaining an acceptable level of fabric whitening, when a fluorescent whitening agent is incorporated into a particulate foam control agent.

Particulate foam control agents often contain a carrier material for the foam control agent to make the foam control agent into a more substantial solid particulate material and facilitate its handling. The particulate foam control agent can then be post-blended as a powder with the rest of the powder detergent composition. The foam control agents are based on silicone antifoams and are well known from the art and have been described in many patent specifications. Also, powder detergent compositions comprising silicone based foam control agents are well known. Foam control agents comprising an encapsulating or protective material are known from EP-A-0,636,684, US-6,165,968, EP-A-0,995,473 and EP-A-0,718,018. The foam control agents disclosed in these references comprise a silicone antifoam, a zeolite carrier for the antifoam, a surface active agent and a polycarboxylate-type binder or encapsulant.

According to the invention there is provided a particulate foam control agent comprising

- (a) from 1 to 30 parts by weight of a silicone antifoam;
- (b) from 45 to 99 parts by weight of a particulate carrier for the antifoam,
- (c) from 2 to 50 parts by weight of a fluorescent whitening agent;

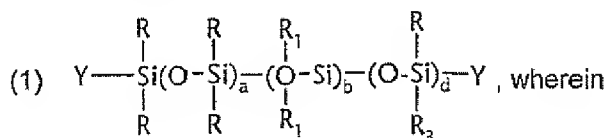
(d) from 1 to 40 parts by weight of a binder .

Preferably the particulate foam control agent also contains from 1 to 60% by weight of the silicone antifoam of a surface active agent (e).

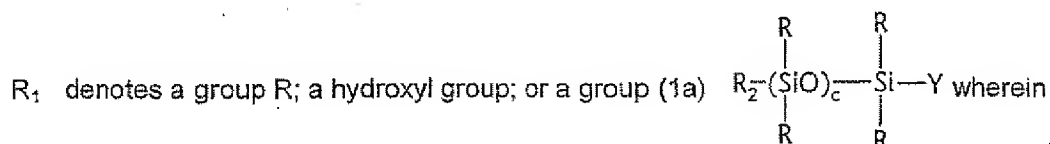
#### Component (a) - silicone antifoam

Silicone antifoams for use in the foam control agents of this invention are known materials and have been described in a number of patent specifications, including those referred to herein. Silicone antifoams are preferably foam regulating compositions comprising a liquid organopolysiloxane polymer and a filler particle the surface of which has been rendered hydrophobic.

Liquid organopolysiloxane polymers that are useful in silicone antifoams are also known and have been described in many patent specifications. Full description of all options is therefore not included but can be found in the many publications including patent application EP-A-578 424. Preferably they are linear or branched polymers having a structure according to the general formula



R denotes a monovalent hydrocarbon group having from 1 to 8 carbon atoms, preferably from 1 to 4 carbon atoms;



R<sub>2</sub> denotes a divalent hydrocarbon, hydrocarbonoxy or siloxane group or oxygen;

R<sub>3</sub> denotes a C<sub>6</sub>-C<sub>35</sub>alkyl group;

Y denotes a group R or a hydroxyl group;

a, b, c and d have a value of 0 or an integer, provided at least one of a and b is an integer, and the total of a+b+c+d has a value such that the viscosity of the organopolysiloxane polymer at 25°C is at least 50 mm<sup>2</sup>/s.

The organopolysiloxane polymers may be linear, in which case  $R_1$  denotes R or a hydroxyl group. It is preferred for the linear organopolysiloxanes that Y denotes a group R and that  $b=0$ .

More preferred are those linear polymers wherein  $d=0$  and wherein at least 80% of all R groups denote an alkyl group having from 1 to 4 carbon atoms, most preferably methyl.

It is most preferred that the linear organo-polysiloxanes are trimethylsiloxane end-blocked polydimethylsiloxanes.

The preferred viscosity of the linear organopolysiloxanes is from 500 to 100,000  $\text{mm}^2/\text{s}$ , more preferably 1000 to 60,000  $\text{mm}^2/\text{s}$  at 25°C.

Organopolysiloxanes that are not linear are also known in the art. The preferred non-linear materials are those having branching in the siloxane chain. These polymers have a structure according to Formula (1), wherein b has a value of at least 1 and  $R_2$  is preferably a divalent siloxane group or an oxygen atom.

Particularly preferred siloxane groups  $R_2$  are small three dimensional siloxane resin particles that may have a number of pending siloxane polymer units.

Branched siloxanes are known and examples of them have been described, together with a method of making them, in a number of patent specifications, i.e. GB 639673, EP 31 532, EP 217 501, EP 273 448, DE 38 05 661 and GB 2 257 709.

Preferred liquid organopolysiloxanes are branched or higher viscosity siloxanes (e.g. having a viscosity above 12,500  $\text{mm}^2/\text{s}$  at 25°C), especially branched siloxanes, as they show an improved ability to control foam in most aqueous surfactant solutions.

Another type of silicone antifoams have been described in patent EP-A-1,075,864. It comprises (A) an organo-polysiloxane material having at least one silicone-bonded substituent of the formula X-Ph, wherein X denotes a divalent aliphatic hydrocarbon group and Ph denotes an optionally substituted aromatic group and (B) an organosilicon resin. The organosilicon resin (B) preferably consists of siloxane units of the formula  $R'_a\text{SiO}_{4a/2}$  wherein

R' denotes a hydroxyl, hydrocarbon or hydrocarbonoxy group, particularly trialkylsiloxy units and  $\text{SiO}_{4/2}$  units, wherein a has a value of from 0.5 to 2.4.

#### Filler particles

Filler particles that are useful in the antifoams for use in foamcontrol agents according to the present invention are also well known and have been described in many publications. They are finely divided particulate materials examples of which include silica, fumed  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ , zinc oxide, magnesium oxide, salts of aliphatic carboxylic acids, reaction products of isocyanates with certain materials, i.e. cyclohexylamine, alkyl amides, for example ethylene or methylene bis stearamide.

Most preferred are silica particles with a surface area as measured by BET measurement of at least  $50 \text{ m}^2/\text{g}$ .

Suitable silica particles may be made according to any of the standard manufacturing techniques for example thermal decomposition of a silicon halide, decomposition and precipitation of a metal salt of silicic acid, i.e. sodium silicate and a gel formation method.

Suitable silicas for use in the antifoams include therefore fumed silica, precipitated silica and gel formation silica. The average particle size of these fillers may range from 0.1 to  $20 \mu\text{m}$ , but is preferably from 0.5 to  $2.5 \mu\text{m}$ .

Where the filler particles are not hydrophobic by themselves, their surface is rendered hydrophobic at least to some extent in order to make the antifoam sufficiently effective in aqueous systems. Rendering the filler particles hydrophobic may be done prior to, or after, dispersing the filler particles in the liquid organopolysiloxane. This can be effected by treatment of the filler particles with treating agents, i.e. reactive silanes or siloxanes, for example dimethyldichlorosilane, trimethylchlorosilane, hexamethyldisilazane, hydroxyl end-blocked and methyl end-blocked polydimethylsiloxanes, siloxane resins or a mixture of one or more of these. Fillers that have already been treated with such compounds are commercially available from many companies, for example Sipemat<sup>®</sup>, D10 from Degussa. The surface of the filler may alternatively be rendered hydrophobic in situ, e.g. after the filler has been dispersed in the liquid organopolysiloxane component. This may be effected by adding to the liquid organopolysiloxane prior to, during or after the dispersion of the filler therein the appropriate amount of treating agent of the kind described above, and heating the mixture to a

temperature above 40°C. The quantity of treating agent to be employed will depend, for example, on the nature of the agent and the filler and will be evident or ascertainable by those skilled in the art. Sufficient should be employed to endow the filler with at least a discernible degree of hydrophobicity. The filler particles are added to the organopolysiloxane in an amount of from 1 to 25% by weight of the antifoam, preferably from 1 to 15%, most preferably from 2 to 8%.

#### Component (b) - Carriers

Examples of carriers that may be used in the foam control agents according to the present invention are zeolites, other silicates, for example magnesium silicate, phosphates, for example powdered or granular sodium tripolyphosphate, sodium sulphate, sodium carbonate, sodium perborate, a cellulose derivative such as sodium carboxymethylcellulose, granulated starch, clay, sodium citrate, sodium acetate, sodium bicarbonate and native starch.

The zeolite may be any of those aluminosilicate materials that are known to be beneficial in detergent powder compositions and have been described in a number of patent specifications. Zeolites are used in detergent compositions as cation exchange components. Suitable zeolite materials include particularly those which are known as zeolite A and have an average formula  $(\text{Na}_2\text{O})_m\text{Al}_2\text{O}_3(\text{SiO}_2)_n(\text{H}_2\text{O})_t$ , wherein m has a value of from 0.9 to 1.3, n has a value of from 1.3 to 4.0 and t has a value of from 1 to 6. Suitable zeolites may be crystalline or amorphous aluminosilicates and have been described in particular in EP 192 442 and EP 329 842 and in the patent specifications that are referred to on page 2 of the latter specification. The zeolites or other carriers are used in an amount of from 45 to 99 parts by weight of the foam control composition, more preferably 50 to 99 %. Suitable zeolites may be pre-treated with e.g. non-ionic surfactants, but are preferably untreated zeolites, as they seem to provide a better stability of the foam control agent when stored in a powder detergent composition.

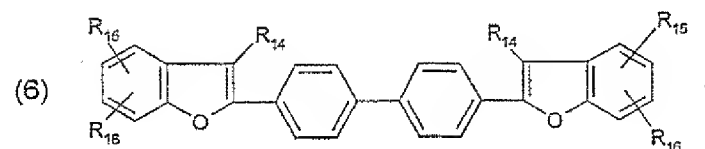
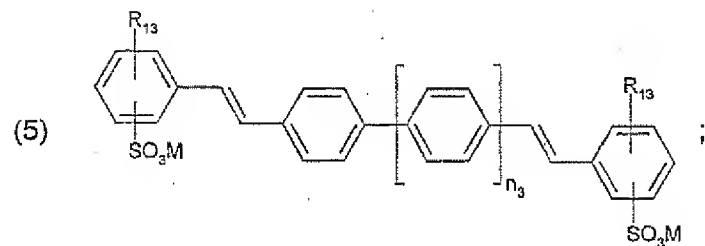
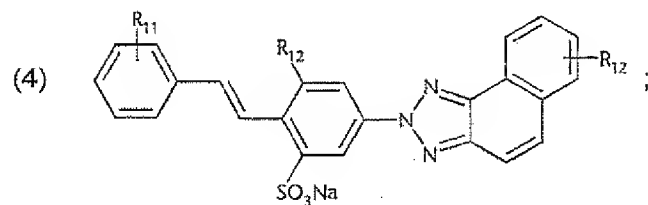
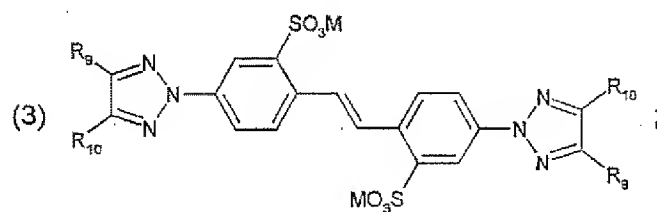
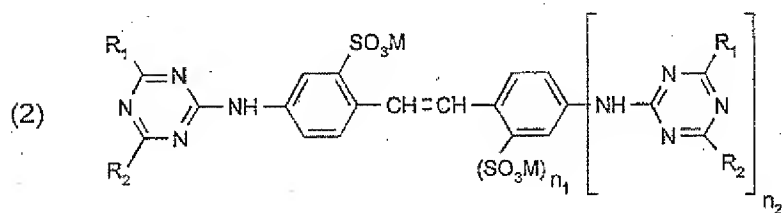
#### Component (e) - Surfactants

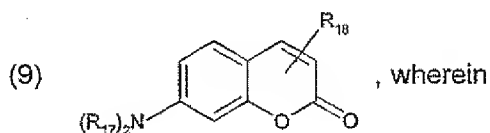
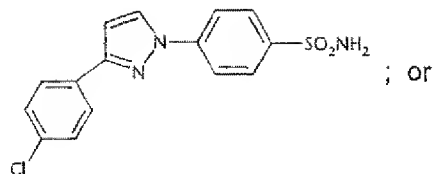
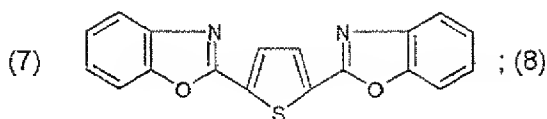
The surfactant used in the foam control agent of the present invention is a substance that will modify the surface tension. If used, it is preferred that the surfactant is deposited on the carrier not later than the silicone antifoam. It is preferred that the surfactant is soluble or dispersible in an aqueous surfactant solution. The surfactant may be selected from anionic, cationic, nonionic or amphoteric materials. Mixtures of one or more of these may also be

used. The surfactant can be an organic surfactant or an organopolysiloxane polyoxyalkylene copolymer. For example, a fatty alcohol ether sulphate or linear alkylbenzene sulphonate may be preferred with a polyacrylic acid binder. The surfactant can be added to the silicone undiluted or in emulsion before the silicone is mixed with the binder, or the surfactant and silicone can successively be added to the binder.

#### Component (c) – Fluorescent whitening agents

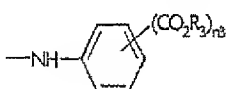
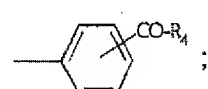
Useful optical brighteners for the invention preferably conform to the formula

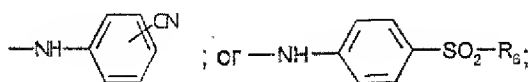




$R_1$  is  $-\text{OH}$ ;  $-\text{Cl}$ ;  $-\text{NH}_2$ ;  $-\text{O}-\text{C}_1-\text{C}_4\text{alkyl}$ ;  $-\text{O-aryl}$ ;  $-\text{NH}-\text{C}_1-\text{C}_4\text{alkyl}$ ;  $-\text{N}(\text{C}_1-\text{C}_4\text{alkyl})_2$ ;

$-\text{N}(\text{C}_1-\text{C}_4\text{alkyl})(\text{C}_1-\text{C}_4\text{hydroxyalkyl})$ ;  $-\text{N}(\text{C}_1-\text{C}_4\text{hydroxyalkyl})_2$ ;  $-\text{NH-aryl}$ ; morpholino; S-

$\text{C}_1-\text{C}_4\text{alkyl(aryl)}$ ; a radical of the formula  ;  ;



$R_2$  is hydrogen; substituted or unsubstituted alkyl or aryl;  $-\text{OH}$ ;  $-\text{Cl}$ ;  $-\text{NH}_2$ ;  $-\text{O}-\text{C}_1-\text{C}_4\text{alkyl}$ ;

$-\text{O-aryl}$ ;  $-\text{NH}-\text{C}_1-\text{C}_4\text{alkyl}$ ;  $-\text{N}(\text{C}_1-\text{C}_4\text{alkyl})_2$ ;  $-\text{N}(\text{C}_1-\text{C}_4\text{alkyl})(\text{C}_1-\text{C}_4\text{hydroxyalkyl})$ ;

$-\text{N}(\text{C}_1-\text{C}_4\text{hydroxyalkyl})_2$ ;  $-\text{NH-aryl}$ ; a radical of the formula  ,  $-\text{OH}$ ;  $-\text{NH}_2$ ;

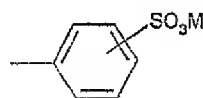
$-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ ;  $-\text{N}[\text{CH}_2\text{CH}(\text{OH})\text{CH}_3]_2$ ;  $-\text{NH}-\text{R}_3$ ;  $-\text{N}(\text{R}_3)_2$ ; or  $-\text{OR}_3$ ;

$R_3$  is substituted or unsubstituted alkyl or aryl; or M;

$R_4$  is hydrogen; substituted or unsubstituted alkyl or aryl; or  $-\text{NR}_7\text{R}_8$ , wherein  $R_7$  and  $R_8$  are independently hydrogen; substituted or unsubstituted alkyl or aryl; or  $R_7$  and  $R_8$  combine with the joining nitrogen atom to form a heterocyclic radical, especially morpholino or piperidino radical;

$R_6$  is hydrogen; or substituted or unsubstituted alkyl or aryl,

$R_9$  and  $R_{10}$  are independently hydrogen;  $\text{C}_1-\text{C}_4\text{alkyl}$ ; phenyl; or a radical of the formula





$R_{11}$  is hydrogen; Cl; or  $\text{SO}_3\text{M}$ ;

$R_{12}$  is  $-\text{CN}$ ;  $-\text{SO}_3\text{M}$ ;  $-\text{S}(\text{C}_1\text{-C}_4\text{alkyl})_2$  or  $\text{S}(\text{aryl})_2$ ;

$R_{13}$  is hydrogen;  $-\text{SO}_3\text{M}$ ;  $-\text{O-C}_1\text{-C}_4\text{alkyl}$ ;  $-\text{CN}$ ;  $-\text{Cl}$ ;  $-\text{COO-C}_1\text{-C}_4\text{alkyl}$ ; or  $\text{CON}(\text{C}_1\text{-C}_4\text{alkyl})_2$ ;

$R_{14}$  is hydrogen;  $-\text{C}_1\text{-C}_4\text{alkyl}$ ;  $-\text{Cl}$ ; or  $-\text{SO}_3\text{M}$ ;

$R_{15}$  and  $R_{16}$  are independently hydrogen;  $\text{C}_1\text{-C}_4\text{alkyl}$ ;  $-\text{SO}_3\text{M}$ ;  $-\text{Cl}$ ; or  $-\text{O-C}_1\text{-C}_4\text{alkyl}$ ;

$R_{17}$  is hydrogen or  $\text{C}_1\text{-C}_4\text{alkyl}$ ;

$R_{18}$  is hydrogen;  $\text{C}_1\text{-C}_4\text{alkyl}$ ;  $-\text{CN}$ ;  $-\text{Cl}$ ;  $-\text{COO-C}_1\text{-C}_4\text{alkyl}$ ;  $-\text{CON}(\text{C}_1\text{-C}_4\text{alkyl})_2$ ; aryl; or  $-\text{O-aryl}$ ;

$\text{M}$  is hydrogen; Na; K; Ca; Mg; ammonium; mono-, di-, tri- or tetra- $\text{C}_1\text{-C}_4\text{alkylammonium}$ ; mono-, di- or tri- $\text{C}_1\text{-C}_4\text{hydroxyalkylammonium}$  or ammonium that is di- or trisubstituted with a mixture of  $\text{C}_1\text{-C}_4\text{alkyl}$  and  $\text{C}_1\text{-C}_4\text{hydroxyalkyl}$  groups; and

$n_1$  and  $n_2$  are independently 0 or 1; and

$n_3$  is 1 or 2.

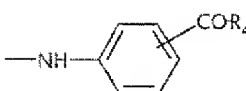
(Substituted or unsubstituted) alkyl  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  is  $\text{C}_1\text{-C}_{12}\text{alkyl}$ , preferably  $\text{C}_1\text{-C}_4\text{alkyl}$ . Alkyl may be branched or unbranched and may be substituted by halogen, for example fluorine, chlorine or bromine,  $\text{C}_1\text{-C}_4\text{alkoxy}$ , for example methoxy or ethoxy, phenyl or carboxyl,  $\text{C}_1\text{-C}_4\text{alkoxycarbonyl}$ , for example acetyl, mono- or di- $\text{C}_1\text{-C}_4\text{alkylamino}$  or  $-\text{SO}_3\text{M}$ .

(Substituted or unsubstituted) aryl  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  is preferably a phenyl or naphthyl group which may be substituted by  $\text{C}_1\text{-C}_4\text{alkyl}$ , for example methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl or tert-butyl,  $\text{C}_1\text{-C}_4\text{alkoxy}$ , for example methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec-butoxy or tert-butoxy, halogen, for example fluorine, chlorine or bromine,  $\text{C}_2\text{-C}_6\text{alkanoylamino}$ , for example acetylamino, propionylamino or butyrylamino, nitro, sulfo or di- $\text{C}_1\text{-C}_4\text{alkylated amino}$ .

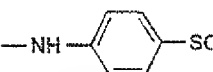
The compounds of the formula (2) are preferably used in neutralized form, i.e.

$\text{M}$  is preferably a cation of an alkali metal, especially sodium, or an amine.

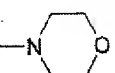
In the compounds of formula (2),  $R_1$  is preferably  $-\text{NH-aryl}$ , preferably  $-\text{NH-phenyl}$ ; or

a radical of the formula , wherein  $R_4$  is as defined above and is

preferably  $C_1$ - $C_4$ alkyl, especially methyl or ethyl, or  $-NR_7R_8$  wherein  $R_7$  and  $R_8$  are each as defined above and are each preferably hydrogen,  $C_1$ - $C_4$ alkyl, especially methyl or ethyl, a morpholino or piperidino radical, most particularly hydrogen, or a radical of the formula

, wherein  $R_6$  is as defined above and is preferably  $-SO_3M$

substituted  $C_1$ - $C_4$ alkyl, especially methyl- or ethyl-substituted  $-SO_3M$ , wherein  $M$  is as defined above and is preferably sodium; and

$R_2$  is preferably ,  $-NH_2$ ,  $-N(CH_2CH_2OH)_2$  or  $-N[CH_2CH(OH)CH_3]_2$ .

The compounds of the formula (2) are preparable under known reaction conditions by reacting cyanuric chloride with appropriate aminostilbenesulfonic acids and with an amino compound capable of introducing an  $R_1$  group and with a compound capable of introducing an  $R_2$  group,  $R_1$  and  $R_2$  being as defined above.

Optical brighteners that are advantageously useful in the present invention are recited below in Table 1 by way of example:

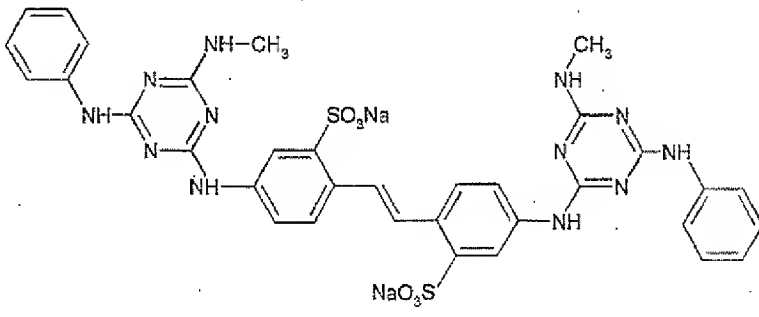
Table 1:	
Compounds of the formula	
(10)	

Table 1:

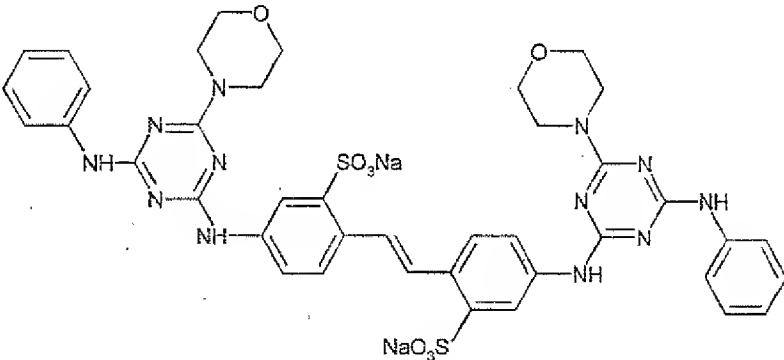
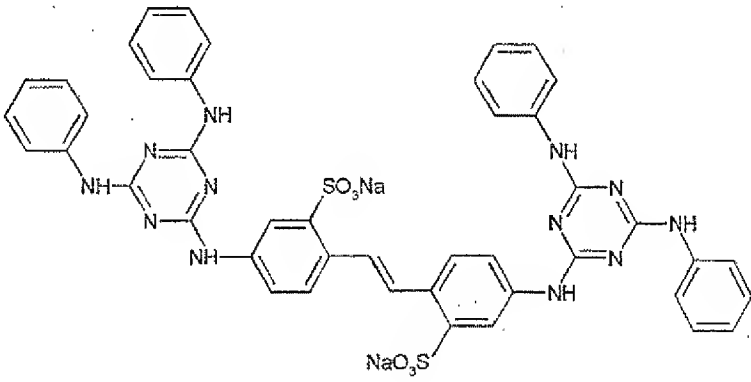
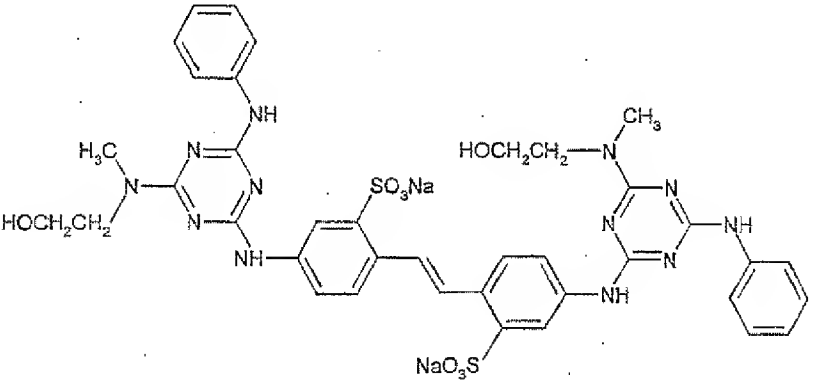
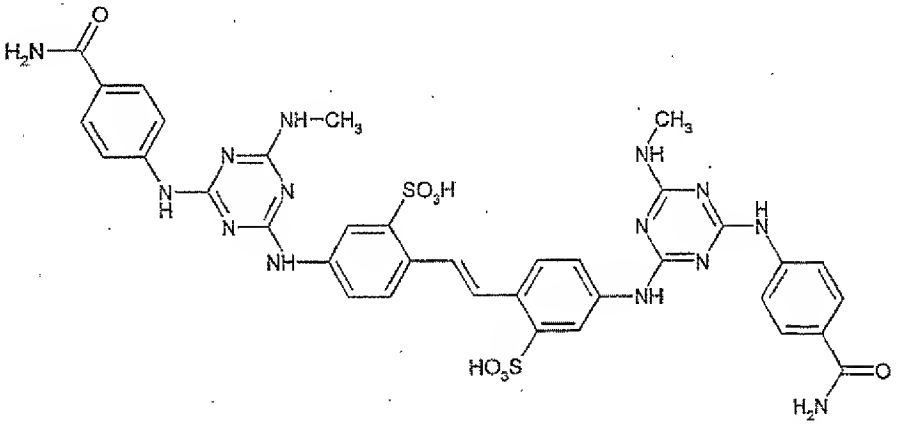
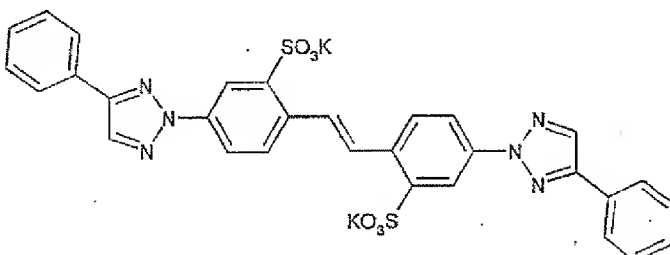
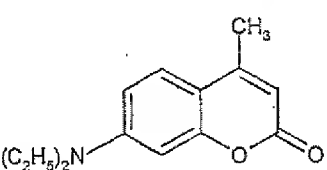
Compounds of the formula	
(11)	
(12)	
(13)	

Table 1:	
Compounds of the formula	
(14)	
(15)	
(16)	
(17)	
(18)	

Table 1:	
Compounds of the formula	
(19)	
(20)	
(21)	

#### Component (d) – binder

Examples of binders which can be used in the foam control agent of the present invention are polycarboxylates, polyoxyalkylene polymers such as polyethylene glycol, which can be applied molten or as an aqueous solution, reaction products of tallow alcohol and ethylene oxide, or polypropylene glycol, cellulose ethers, particularly water-soluble or water-swelling cellulose ethers such as sodium carboxymethylcellulose, gelatin, agar, microcrystalline waxes, fatty acids or fatty alcohols having 12 to 20 carbon atoms and a melting point in the

range 45 to 80°C, a monoester of glycerol and such a fatty acid, a mixture of a water insoluble wax having a melting point in the range from above 55°C to below 100°C and a water-insoluble emulsifying agent, glucose or hydrogenated glucose.

Polycarboxylate binders are preferred. The polycarboxylate-type binder preferably has an acid pH value and even more preferably a pH of 5 or less when dissolved in water.

The pH of the polycarboxylate-binder is the pH of a solution of 10% by weight of the polycarboxylate-binder in water, measured at 296K (23°C).

The binder (component (d)) for use in the present invention allows to obtain an improved encapsulation or protection of the antifoam and the optical brightener, which is not adversely affected by a storing of the foam control agent for prolonged periods of time, even under humid conditions. The specified polycarboxylate-type binder achieves a strong interaction between a zeolite carrier material and the polycarboxylate binder. The stronger interaction between the zeolite carrier material and the polycarboxylate binder appears to result in an increased bond strength or cohesion within the polycarboxylate binder layer, thus providing a better protection of the silicone antifoam. In that way, the ability of moisture to break and open the encapsulating or protecting binder layer, which would result in an undesired release of the silicone anti-foam and the optical brightener from the foam control agent in a too early stage and absorption by or spreading of the silicone oil from the anti-foam over the detergent powder, can be significantly reduced. The improved encapsulation or protection has namely been found capable of showing an increased resistance towards moisture, thus preventing an undesired release of the antifoam and the optical brightener when storing the foam control agent for a prolonged period of time, even in humid conditions as a result of the increased interaction between the zeolite carrier and the polycarboxylate-type binder. In that way a foam control agent can be obtained with an improved encapsulation of the antifoam control agent, which results in an increased storage stability of the foam control agent.

Polycarboxylate materials are known as dispersing agents in detergent powders and are water soluble polymers, homopolymers, copolymers or salts thereof. They have at least 60% by

weight of segments with the general formula  $\begin{array}{c} \text{A} \quad \text{Z} \\ | \quad | \\ (\text{C} - \text{C})_t \\ | \quad | \\ \text{Q} \quad \text{COOM} \end{array}$ , wherein

A, Q and Z are each selected from the group consisting of hydrogen, methyl, carboxy, carboxymethyl, hydroxy and hydroxymethyl;  
M is hydrogen; alkali metal; ammonium or substituted ammonium; and  
t is from 30 to 400.

Preferably A is hydrogen or hydroxy, Q is hydrogen or carboxy, and Z is hydrogen.

Suitable polymeric polycarboxylates include polymerised products of unsaturated monomeric acids, i.e. acrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, acetic acid, mesaconic acid, tetraconic acid and methylene malonic acid. Examples of preferred polycarboxylates include polyacrylic acid or a partial sodium salt thereof or a copolymer of acrylic acid, for example a copolymer with maleic anhydride.

The copolymerisation with lesser amounts of monomeric materials comprising no carboxylic acid, i.e. vinylmethyl, vinylmethylethers, styrene and ethylene, is not detrimental to the use of the polycarboxylates in the foam control agents of the present invention. Depending on the type of polycarboxylate this level can be kept low or levels can be up to about 40% by weight of the total polymer or copolymer.

Preferred polycarboxylates are those which have a molecular weight of no more than 9000.

More preferred polycarboxylates have a molecular weight of between 1000 and 6000. It has namely been found that the efficiency of the protection or encapsulation by the polyacrylate-type binder varies with its molecular weight.

Polycarboxylates with a molecular weight of no more than 9000 show an optimal mobility, so that an optimal encapsulation or protection can be achieved.

Particularly suitable polymeric polycarboxylates are the polyacrylates with an average viscosity at 23°C in mPa.s from 50 to 10,000, preferably from 1,500 to 8,000.

Carboxylates may be supplied in powder or liquid form. They may be liquid at room temperature or may be supplied as aqueous solutions. The latter are preferred as they facilitate the manufacture of the foam control agents according of the present invention with

conventional spray applications.

#### Detergent composition

The present invention also relates to a detergent composition in powder form which comprises 100 parts by weight of a detergent component and sufficient of a foam control agent according to the first aspect of the invention to give 0.02 to 5 parts by weight of the silicone antifoam comprised in the foam control agent.

Suitable detergent components are well known in the art and have been described in numerous publications. The components comprise an active detergent, organic and/or inorganic builder salts and other additives and diluents. The active detergent may comprise organic detergent surfactants of the anionic, cationic, non-ionic or amphoteric type, or mixtures thereof. Suitable anionic organic detergent surfactants include alkali metal soaps of higher fatty acids, alkyl aryl sulphonates for example sodium dodecyl benzene sulphonate, long chain (fatty) alcohol sulphates, olefin sulphates and sulphonates, sulphated mono-glycerides, sulphated esters, sulphosuccinates, alkane sulphonates, phosphate esters, alkyl isothionates, sucrose esters and fluorosurfactants. Suitable cationic organic detergent surfactants include alkylamine salts, quaternary ammonium salts, sulphonium salts and phosphonium salts. Suitable non-ionic detergent surfactants include condensates of ethylene oxide with a long chain (fatty) alcohol or (fatty) acid, for example C<sub>14</sub>-C<sub>15</sub>alcohol condensed with 7 moles of ethylene oxide (Dobanol® 45-7), condensates of ethylene oxide with an amine or amide, condensation products of ethylene and propylene oxides, fatty acid alkylol amide and fatty amine oxides. Suitable amphoteric organic detergent surfactants include imidazoline compounds, alkylaminoacid salts and betaines. Examples of inorganic components are phosphates, polyphosphates, silicates, carbonates, sulphates, oxygen releasing compounds such as sodium perborate and other bleaching agents and aluminosilicates, e.g. zeolites. Examples of organic components are anti-redeposition agents such as carboxymethylcellulose (CMC), brighteners, chelating agents, such as ethylene diamine tetra-acetic acid (EDTA) and nitrilotriacetic acid (NTA), enzymes and bacteriostats. Other optional components include colorants, dyes, perfumes, softeners, clays, some of which may be encapsulated. Materials suitable for the detergent component are well known to the person skilled in the art and are described in many text books as well as other publications.



### Process of preparation

The present invention also relates to a method for the preparation of a foam control agent which comprises depositing from 1 to 30 parts by weight of a silicone antifoam and from 2 to 50 parts by weight of a fluorescent whitening agent, on from 45 to 99 parts by weight of a particulate carrier, together with or after from 1 to 60% by weight of the silicone antifoam of a surface active agent, and from 1 to 40 parts by weight of a binder, have been deposited on the carrier.

It is preferred that a polycarboxylate binder and the surface active agent are deposited onto a zeolite carrier not later than the silicone antifoam and the fluorescent whitening agent to achieve optimum storage stability of the foam control agent and fluorescent whitening agent.

An even more preferred method is where a mixture of the four components (silicone antifoam, surface active agent, fluorescent whitening agent and binder) is made according to any of the known methods, and this mixture deposited onto the carrier

The premix can be made by simply mixing the ingredients, preferably with reasonable shear or high shear. Where one or more ingredients are solid or waxy materials, or materials of high viscosity, it may be beneficial to heat the mixture to melt or reduce the working viscosity of the mix. Alternatively the premix of the components may be diluted with a solvent, e.g. a low viscosity siloxane polymer, cyclic siloxane polymer, organic solvent or even by making a dispersion in water.

Depositing the mix onto a carrier can be done in a number of ways. Conventional procedures of making powders are particularly useful for making the particulate foam control agent. These include depositing of a previously prepared mixture of all of the two, three or four components onto the zeolite which is the most preferred method.

One particularly useful way of depositing the components onto the carrier is by spraying one or more of these onto the carrier which may be present in a drum mixer, fluidised bed etc. This may be done at room temperature or at elevated temperature, which is particularly useful if one wants to evaporate some or all of the solvent during the process. In one process the carrier powder is mixed with the premix of all the other components, e.g. in a high shear mixer, e.g. Eirich® pan granulator, Schugi® mixer, Paxeson-Kelly® twin-core blender, Loedige® ploughshare mixer, Aeromatic® fluidised bed granulator or Pharma® type drum

mixer. The deposition may be done by pouring the mixture into the mixer, as an alternative to spraying as described above.

In an alternative process, a fluorescent whitening agent which is a solid powder can be mixed with the carrier. The silicone antifoam and binder can be deposited on the mixture of carrier and fluorescent whitening agent.

The process of the invention uses from 1 to 30 parts by weight of silicone antifoam and from 45 to 99 parts by weight of zeolite. If a lower amount of silicone antifoam are to be used this would make the foam control agent less effective as the silicone antifoam would be too thinly distributed on the carrier material. Higher amounts than 30 parts of silicone antifoam are possible in theory, but are not practical, as this would render the dispersion of the foam control agent in the powder detergent more difficult and one could not be sure that each measure of powder detergent would incorporate the correct amount of silicone antifoam. Higher levels would also possibly result in a more tacky material which would not be granulated very easily.

Thus use of 1 to 60% of surface active agent by weight based on the weight of the silicone antifoam is chosen for efficiency reasons as well as to minimize the amount of material which is to be introduced in the powder detergent which is not per se beneficial to the cleaning efficiency of the detergent composition. It is more preferred to use 5 to 60 % by weight, especially 5 to 35 % by weight, based on the weight of the silicone antifoam.

The amount of binder, for example polycarboxylate, is from 1 to 40 parts by weight of the composition. Preferably the binder is used in amounts of from 1 to 30 parts, most preferably 4 to 25 parts by weight.

The invention is further illustrated in the following examples. All parts and percentages are given by weight unless otherwise indicated.

#### EXAMPLE 1

A co-granule was prepared by mixing approximately 62 parts of zeolite 4A HA, a zeolite manufactured by Zeoline, with approximately 15.9 parts of a Sokalan PA25 PN polycarboxylate binder material provided by BASF, approximately 14.2 parts of a silicone antifoam, comprising a branched polymethylsiloxane polymer and hydrophobic silica, approximately 5.9 parts of a solution of an organic surfactant being a Sodium Lauryl ether Sulfate solution provided by IfraChem under the name Ifrapon LOS 2N 70 and approximately 39.4 parts of a Tinopal DMS Slurry 36 provided by Ciba. The mixture was prepared by pure mechanically mixing the antifoam, the surfactant, binder and optical brightener together and pouring the mixture very slowly into a drum mixer in which the zeolite was placed. The mixture was stirred continuously until a particulate material was obtained. The obtained granule is then dried in a fluidized bed for 20 minutes.

#### EXAMPLE 2

A co-granule was prepared by mixing approximately 62.3 parts of zeolite 4A HA, a zeolite manufactured by Zeoline, with approximately 15.8 parts of a Sokalan PA25 PN polycarboxylate binder material provided by BASF, approximately 14.2 parts of a silicone antifoam comprising an organopolysiloxane material having at least one silicon-bonded substituent of the formula X-Ph, wherein X denotes a divalent aliphatic hydrocarbon group and Ph denotes an optionally substituted aromatic group, an organosilicon resin and a hydrophobic filler, approximately 4.1 parts of an organic surfactant being a Sodium N-Lauroyl Sarcosinate solution provided under the name Crodasinc LS35 by Croda and approximately 39.3 parts of a Tinopal DMS Slurry 36 provided by Ciba. The mixture was prepared by pure mechanically mixing the antifoam, the surfactant, binder and optical brightener together and pouring the mixture very slowly into a drum mixer in which the zeolite was placed. The mixture was stirred continuously until a particulate material was obtained. The obtained granule is then dried in a fluidized bed for 20 minutes.

#### EXAMPLE 3

A co-granule was prepared by mixing approximately 78.95 parts of zeolite 4A HA, a zeolite manufactured by Zeoline, with approximately 14.8 parts of a Sokalan PA25 PN polycarboxylate binder material provided by BASF, approximately 12.6 parts of a silicone antifoam comprising an organopolysiloxane material having at least one silicon-bonded substituent of the formula X-Ph, wherein X denotes a divalent aliphatic hydrocarbon group and Ph denotes

an optionally substituted aromatic group, an organosilicon resin and a hydrophobic filler, and approximately 3 parts of an organic surfactant being a Sodium N-Lauroyl Sarcosinate solution provided under the name Crodasinc LS35 by Croda. The mixture was prepared by pure mechanically mixing the antifoam, the surfactant and the binder and pouring the mixture very slowly into a drum mixer in which the zeolite was placed. The mixture was stirred continuously until a particulate material was obtained. The obtained granule is then postboated in a fluidized bed with Tinopal CBS-CL provided by Ciba to achieve a final concentration of active optical brightener in the granule of about 6 %. The granule is dried in the fluidized bed.

#### EXAMPLE 4

A co-granule was prepared by mixing approximately 80.7 parts of zeolite 4A MA, a zeolite manufactured by Zeoline, with approximately 10.4 parts of a Sokalan PA25 PN polycarboxylate binder material provided by BASF, approximately 7 parts of a silicone antifoam, comprising a branched polymethylsiloxane polymer and hydrophobic silica, approximately 3 parts of a solution of an organic surfactant being a Sodium Lauryl ether Sulfate solution provided by IfraChem under the name Ifrapon LOS 2N 70 and approximately 20.8 parts of a Tinopal CBS SP Slurry 33 provided by Ciba. The mixture was prepared by pure mechanically mixing the antifoam, the surfactant, binder and optical brightener together and pouring the mixture very slowly into a drum mixer in which the zeolite was placed. The mixture was stirred continuously until a particulate material was obtained. The obtained granule is then dried in a fluidized bed for 20 minutes.

#### EXAMPLE 5

A co-granule was prepared by mixing approximately 79.4 parts of zeolite 4A MA, a zeolite manufactured by Zeoline, with approximately 10.4 parts of a Sokalan PA25 PN polycarboxylate binder material provided by BASF, approximately 7.1 parts of a silicone antifoam comprising an organopolysiloxane material having at least one silicon-bonded substituent of the formula X-Ph, wherein X denotes a divalent aliphatic hydrocarbon group and Ph denotes an optionally substituted aromatic group, an organosilicon resin and a hydrophobic filler, approximately 3 parts of a solution of an organic surfactant being a Sodium Lauryl ether Sulfate solution provided by IfraChem under the name Ifrapon LOS 2N 70 and approximately 20.9 parts of a Tinopal DMS Slurry 36 provided by Ciba. The mixture was prepared by pure mechanically mixing the antifoam, the surfactant, binder and optical brightener together and pouring the mixture very slowly into a drum mixer in which the zeolite was placed. The

mixture was stirred continuously until a particulate material was obtained. The obtained granule is then dried in a fluidized bed for 20 minutes.

#### EXAMPLE 6

A co-granule was prepared by mixing approximately 79.3 parts of zeolite 4A MA, a zeolite manufactured by Zeoline, with approximately 10.4 parts of a Sokalan PA25 PN polycarboxylate binder material provided by BASF, approximately 7.1 parts of a silicone antifoam, comprising a branched polymethylsiloxane polymer and hydrophobic silica, approximately 3 parts of a solution of an organic surfactant being a Sodium Lauryl ether Sulfate solution provided by IffaChem under the name Iffrapon LOS 2N 70 and approximately 20.9 parts of a Tinopal DMS Slurry 36 provided by Ciba. The mixture was prepared by pure mechanically mixing the antifoam, the surfactant, binder and optical brightener together and pouring the mixture very slowly into a drum mixer in which the zeolite was placed. The mixture was stirred continuously until a particulate material was obtained. The obtained granule is then dried in a fluidized bed for 20 minutes.

#### Comparative EXAMPLE

A granule was prepared by mixing approximately 85 parts of zeolite 4A MA, a zeolite manufactured by Zeoline, with approximately 14 parts of a Sokalan PA25 PN polycarboxylate binder material provided by BASF, and approximately 22.1 parts of a Tinopal DMS Slurry 36 provided by Ciba. The mixture was prepared by pure mechanically mixing the binder and the optical brightener together and pouring the mixture very slowly into a drum mixer in which the zeolite was placed. The mixture was stirred continuously until a particulate material was obtained. The obtained granule is then dried in a fluidized bed for 20 minutes.

The granules prepared in examples 5, 6 and the comparative example were tested for whiteness index and spotting behavior. The level of active optical brightener has been analytically measured in the 3 granules and is respectively 10.44 %, 10.4 % and 10.8 %.

#### Determination of Whiteness Delivery

The whiteness performance is evaluated on bleached cotton by washing under laboratory scale conditions at the following European washing conditions:

Detergent type: Standard Detergent ECE77  
 Detergent dosage: 100g per kg  
 Formulations (5a)-(5c): 1% based on the detergent  
 Liquor ratio: 10 to 1  
 Washing temperature: 40°C  
 Washing time: 15 minutes  
 Test fabric: bleached cotton renforcé  
 Wash cycles: 1 – 3 and 5 cycles  
 Drying: indoor i.e. by ironing

The results are listed in Table 2.

<u>Table 2:</u>				
<u>formulation</u>	<u>Equivalent FWA concentration compound of formula (11)</u>	<u>Whiteness Ganz</u>		
		<u>1<sup>st</sup> cycle</u>	<u>3<sup>rd</sup> cycle</u>	<u>5<sup>th</sup> cycle</u>
Comparative example	0.15%	152	192	206
Example 5	0.15%	147	187	200
Example 6	0.16%	149	188	202

The formulations show a good whiteness effect.

#### Determination of the spotting/ leveling behavior

##### Conditions:

- 1.Spotting: 30mg FWA compounds are spread on the upper layer of 10g bleached cotton fabric folded in 4 layers, wetted with 50ml water.
- 2.Washing: 100 g standard detergent ECE77 per kg fabric, liqor ratio , 10 to 1, 15 minutes washing at 40°C on bleached cotton renforcé after 5 minutes contact time of the FWA compounds on the wet fabric.

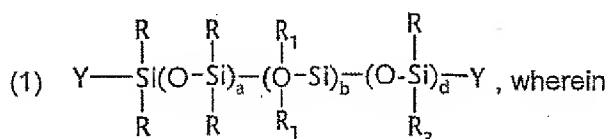
The spotting/ leveling behavior is evaluated under lab test conditions according to the conditions mentioned on Table 3:

<u>Table 3: Spotting behavior of FWA containing foamcontrol agents</u>	
<u>formulation</u>	<u>Visual evaluation under day- light conditions</u>
Comparative Example	No spotting
Example 5	No spotting
Example 6	No spotting

According to the spotting tests done under lab scale conditions, the formulations do not cause any spotting.

Claims:

1. A particulate foam control agent comprising
  - (a) from 1 to 30 parts by weight of a silicone antifoam;
  - (b) from 45 to 99 parts by weight of a particulate carrier for the antifoam,
  - (c) from 2 to 50 parts by weight of a fluorescent whitening agent; and
  - (d) from 1 to 40 parts by weight of a binder.
2. A particulate foam control agent as claimed in claim 1, wherein component (a) is a liquid organopolysiloxane polymer and a filler particle the surface of which has been rendered hydrophobic, the organopolysiloxane being a linear or branched polymer having a structure according to formula



R denotes a monovalent hydrocarbon group having from 1 to 8 carbon atoms, preferably from 1 to 4 carbon atoms;

R<sub>1</sub> denotes a group R; a hydroxyl group; or a group (1a)  $\text{R}_2 - (\text{SiO})_c - \underset{\text{R}}{\overset{\text{R}}{\text{Si}}} - \text{Y}$ , wherein

R<sub>2</sub> denotes a divalent hydrocarbon, hydrocarbonoxy or siloxane group or oxygen;

R<sub>3</sub> denotes a C<sub>9</sub>-C<sub>35</sub> alkyl group;

Y denotes a group R or a hydroxyl group;

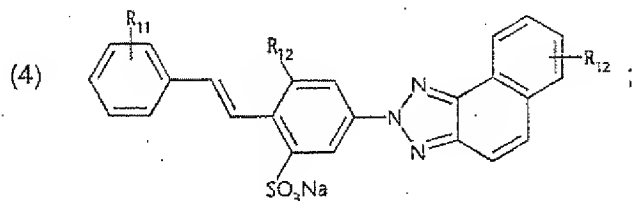
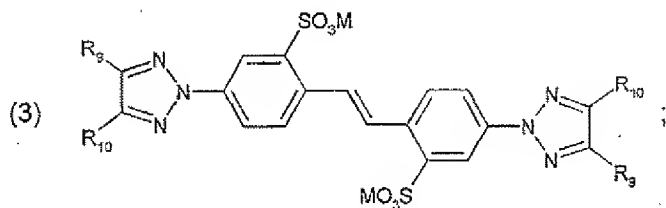
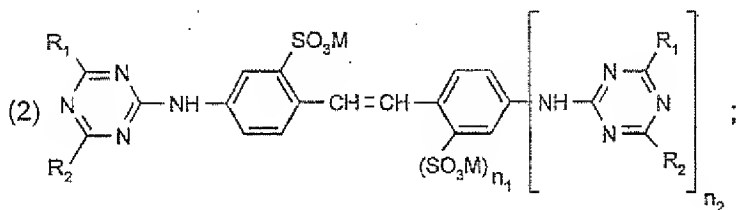
a, b, c and d have a value of 0 or an integer, provided at least one of a and b is an integer, and the total of a+b+c+d has a value such that the viscosity of the organopolysiloxane polymer at 25°C is at least 50 mm<sup>2</sup>/s.

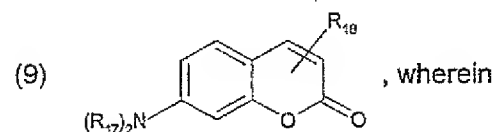
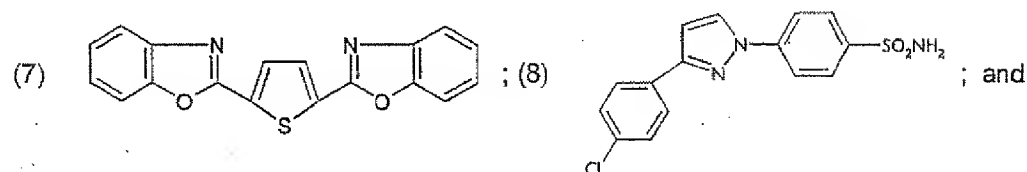
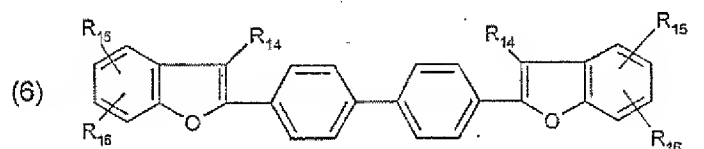
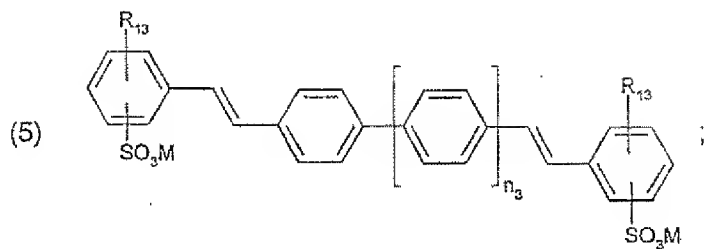
3. A particulate foam control agent as claimed in claim 1 or 2, wherein component (a) comprises (A) an organo-polysiloxane material having at least one silicone-bonded substituent of the formula X-Ph, wherein X denotes a divalent aliphatic hydrocarbon group and Ph denotes an optionally substituted aromatic group and (B) an organosilicon resin and (C) a hydrophobic filler. The organosilicon resin (B) preferably consists of siloxane units of the formula R'<sub>a</sub>SiO<sub>4-2/2</sub> wherein R' denotes a hydroxyl, hydrocarbon or



hydrocarboxy group, particularly trialkylsiloxy units and  $\text{SiO}_{4/2}$  units, wherein a has a value of from 0.5 to 2.4.

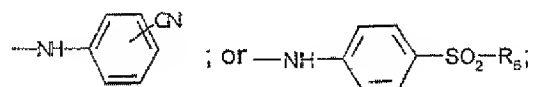
4. A particulate foam control agent as claimed in any of claims 1 to 3, wherein the particulate foam control agent (a) additionally contains from 1 to 60% by weight of the silicone antifoam of a surface active agent (component (e)).
5. A particulate foam control agent as claimed in any of claims 1 to 4, wherein the carrier (component (b)) is a zeolite.
6. A particulate foam control agent as claimed in claim 5, wherein component (b) is a zeolite A type and has an average formula  $(\text{Na}_2\text{O})_m\text{Al}_2\text{O}_3(\text{SiO}_2)_n(\text{H}_2\text{O})_t$ , wherein m has a value of from 0.9 to 1.3, n has a value of from 1.3 to 4.0 and t has a value of from 1 to 6.
7. A particulate foam control agent as claimed in any of claims 1 to 6, wherein the fluorescent whitening agent (component (c)) is selected from the compounds of formulae





$R_1$  is  $-\text{OH}$ ;  $-\text{Cl}$ ;  $-\text{NH}_2$ ;  $-\text{O}-\text{C}_1-\text{C}_4$  alkyl;  $-\text{O}$ -aryl;  $-\text{NH}-\text{C}_1-\text{C}_4$  alkyl;  $-\text{N}(\text{C}_1-\text{C}_4 \text{ alkyl})_2$ ;  $-\text{N}(\text{C}_1-\text{C}_4 \text{ alkyl})(\text{C}_1-\text{C}_4 \text{ hydroxyalkyl})$ ;  $-\text{N}(\text{C}_1-\text{C}_4 \text{ hydroxyalkyl})_2$ ;  $-\text{NH}$ -aryl; morpholino;

$\text{S}-\text{C}_1-\text{C}_4$  alkyl(aryl); a radical of the formula



$R_2$  is hydrogen; substituted or unsubstituted alkyl or aryl;  $-\text{OH}$ ;  $-\text{Cl}$ ;  $-\text{NH}_2$ ;  $-\text{O}-\text{C}_1-\text{C}_4$  alkyl;  $-\text{O}$ -aryl;  $-\text{NH}-\text{C}_1-\text{C}_4$  alkyl;  $-\text{N}(\text{C}_1-\text{C}_4 \text{ alkyl})_2$ ;  $-\text{N}(\text{C}_1-\text{C}_4 \text{ alkyl})(\text{C}_1-\text{C}_4 \text{ hydroxyalkyl})$ ;

$-\text{N}(\text{C}_1-\text{C}_4 \text{ hydroxyalkyl})_2$ ;  $-\text{NH}$ -aryl; a radical of the formula

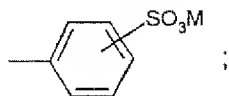
$-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ ;  $-\text{N}[\text{CH}_2\text{CH}(\text{OH})\text{CH}_3]_2$ ;  $-\text{NH}-\text{R}_3$ ;  $-\text{N}(\text{R}_3)_2$  or  $-\text{OR}_3$ ;

$R_3$  is substituted or unsubstituted alkyl or aryl; or M;

$R_4$  is hydrogen; substituted or unsubstituted alkyl or aryl; or  $-NR_7R_8$ , wherein  $R_7$  and  $R_8$  are independently hydrogen; substituted or unsubstituted alkyl or aryl; or  $R_7$  and  $R_8$  combine with the joining nitrogen atom to form a heterocyclic radical;

$R_6$  is hydrogen; or substituted or unsubstituted alkyl or aryl;

$R_9$  and  $R_{10}$  are independently hydrogen;  $C_1$ - $C_4$ alkyl; phenyl; or a radical of the formula



$R_{11}$  is hydrogen; Cl; or  $SO_3M$ ;

$R_{12}$  is  $-CN$ ;  $-SO_3M$ ;  $-S(C_1-C_4alkyl)_2$ ; or  $S(aryl)_2$ ;

$R_{13}$  is hydrogen;  $-SO_3M$ ;  $-O-C_1-C_4alkyl$ ;  $-CN$ ;  $-Cl$ ;  $-COO-C_1-C_4alkyl$ ; or  $CON(C_1-C_4alkyl)_2$ ;

$R_{14}$  is hydrogen;  $-C_1-C_4alkyl$ ;  $-Cl$ ; or  $-SO_3M$ ;

$R_{15}$  and  $R_{16}$  are independently hydrogen;  $C_1-C_4alkyl$ ;  $-SO_3M$ ;  $-Cl$ ; or  $-O-C_1-C_4alkyl$ ;

$R_{17}$  is hydrogen; or  $C_1-C_4alkyl$ ;

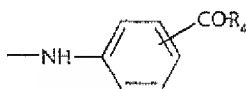
$R_{18}$  is hydrogen;  $C_1-C_4alkyl$ ;  $-CN$ ;  $-Cl$ ;  $-COO-C_1-C_4alkyl$ ;  $-CON(C_1-C_4alkyl)_2$ ; aryl; or  $-O$ -aryl;

$M$  is hydrogen; Na; K; Ca; Mg; ammonium; mono-, di-, tri- or tetra- $C_1$ - $C_4$ alkylammonium; mono-, di- or tri- $C_1$ - $C_4$ hydroxyalkylammonium; or ammonium that is di- or trisubstituted with a mixture of  $C_1$ - $C_4$ alkyl and  $C_1$ - $C_4$ hydroxyalkyl groups; and

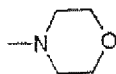
$n_1$  and  $n_2$  are independently 0 or 1; and

$n_3$  is 1 or 2.

8. A particulate foam control agent as claimed in claim 7, wherein component (c) corresponds to formula (2), wherein

$R_1$  is preferably  $-NH$ -aryl; or a radical of the formula , wherein  $R_4$  is

$C_1$ - $C_4$ alkyl; or  $-NR_7R_8$ , wherein  $R_7$  and  $R_8$  are hydrogen;  $C_1$ - $C_4$ alkyl; a morpholino or piperidino radical; and is preferably sodium; and

$R_2$  is ,  $-NH_2$ ,  $-N(CH_2CH_2OH)_2$  or  $-N[CH_2CH(OH)CH_3]_2$ .

9. A particulate foam control agent as claimed in any of claims 1 to 8, wherein the binder (component (d)) is a polycarboxylate
10. A particulate foam control agent as claimed in claim 9, wherein the polycarboxylate binder has a molecular weight of no more than 9000.
11. A particulate foam control agent as claimed in any of claims 1 to 10, wherein the polycarboxylate binder (component (d)) has been acidified to a pH of 6.5 or less, prior to the preparation of the foam control agent.
12. A detergent composition in powder form comprising 100 parts by weight of a detergent component and a sufficient amount of a particulate foam control agent comprising
  - (a) from 1 to 30 parts by weight of a silicone antifoam,
  - (b) from 45 to 99 parts by weight of a zeolite carrier for the antifoam,
  - (e) from 1 to 60% by weight of the silicone antifoam of a surface active agent which has been deposited on the zeolite carrier not later than the silicone
  - (c) from 2 to 50 parts by weight of a fluorescent whitening agent; and
  - (d) from 1 to 40 parts by weight of a polycarboxylate binder or encapsulant,to give 0.02 to 5 parts by weight of the silicone antifoam comprised in the foam control agent.
13. A method for the preparation of a foam control agent which comprises depositing from 1 to 30 parts by weight of a silicone antifoam and 2 to 50 parts by weight of a fluorescent whitening agent on 45 to 99 parts by weight of a zeolite carrier, said silicone antifoam and fluorescent whitening agent being deposited together with or after the deposition of 1 to 60% by weight of the silicone antifoam of a surface active agent and 1 to 40 parts by weight of a polycarboxylate binder or encapsulant.

## INTERNATIONAL SEARCH REPORT

Int. Application No.  
PCT/EP 03/03727

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D19/04 C11D3/42 C11D3/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 636 684 A (DOW CORNING) 1 February 1995 (1995-02-01) cited in the application page 8, line 23 - line 26; claims 1-3 page 8, line 42 - line 43	1, 2, 4-6, 9, 12, 13
A	WO 00 20546 A (THE PROCTER & GAMBLE) 13 April 2000 (2000-04-13) page 9, line 15 - page 10, line 19; claims 1, 3 page 11, line 8 - line 10 page 13, line 1 - line 9 page 16, line 8 - line 17 page 16, line 35 - line 9 page 16, line 35 - page 17, line 9 -- -/--	1-4, 9, 10, 12, 13

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

22 September 2003

Date of mailing of the international search report

30/09/2003

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## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 03/03727

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A	GB 2 315 765 A (THE PROCTER & GAMBLE COMPANY) 11 February 1998 (1998-02-11) page 35, line 3 -page 36, line 5 page 41, line 11 -page 42, line 22 page 46; examples A,B ---	1,2,4-8, 12,13
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